THE DETERMINATION OF THE ACIDITY VALUE IN CELLULOSE TRIACETATE DOPE

A THESIS

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ABSTRACT

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This research was concerned with the development of a new method or modification of an existing method for the determination of the acidity in cellulose triacetate dope. Several indicators with concentration ranges of 0.02% to 1. 0% were used in order to elucidate which one would yield the sharpest change. Indicators used were Bromothymol Blue, Phenol Red, Cresol Purple and Thymolphthalein. The results indicated that Phenol Red yielded the best visible color.

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INTRODUCTION

Cellulose acetate is a well-known derivative of cellulose which has been found to be useful as a fiber, film and a plastic coating. However, since it is not readily soluble in organic solvents, cellulose acetate was not adopted as a fiber for some time. It was in the early 1900's that Miles and Von Bayer[1] discovered that solubility could be achieved more easily if some of the acetyl groups were removed by acid hydrolysis. This idea was commercialized by Camille and Dreyfus.[1] Cellulose triacetate which is similar to acetate in chemical structure, appeared as a fiber in the late 1940's and was commercialized in 1954.[1] The term triacetate is used when at least ninety-two percent of the hydroxyl groups are acetylated. Acetate on the other hand, normally has about eighty-three percent of the hydroxyls acetylated.[1]

The production of cellulose acetate and cellulose triacetate involves the following steps. The purified cellulose, in the form of wood pulp is shredded into very small particles as it is run through attrition mills. These particles are blown into a cyclone where the air is removed, and then into a pretreater. In the pretreater, acetic acid is added. At the same time, a mixture containing acetic anhydride, acetic acid and sulfuric acid is then added to the crystallizer. The materials in the pretreater are mixed with the mixture in the acetylator to form a viscous solution. This is called acid dope. The acetate acid dope is transferred to a vessel called a ripener where it is heated or ripened, until the dope reaches a desired acetyl value. At this point the sulfuric acid is completely neutralized.

The ripening process is omitted for triacetate acid dope. The triacetate dope goes through a desulfation step directly after the acetylation process. When fully desulfated, the sulfuric acid in this dope is completely neutralized. The dope is then pumped to retention tanks. The dope is passed from the retention tank to a precipitator where it is mixed with acetic acid or a weak acid solution that precipitates flake from dope. The dope then passes through a hardening tank and across a shaker screen. A large amount of the excess acid is removed by the screen. This excess acid is piped to acid recovery.

Next, the materials pass through a hammer mill. The purpose of the hammer mill is to break up any large pieces that may have come through the hardening tank. Two wash stages follow to make sure the dope is acid free. The dope is then carried through a dryer. The dried material produced is known as flake. The flake is dissolved in solvent mixtures. The cellulose acetate flake is dissolved in a solvent mixture of acetone plus two percent water and the cellulose triacetate is dissolved in a mixture of methylene chloride plus nine percent methanol. From the mixtures a dope is formed.

There are four types of dope. Two of the four, called "dull" dope, have the pigment titanium dioxide added to them and two have no pigment added and are called "bright" dope. There is a "dull" and "bright" cellulose triacetate as well as a "dull" and "bright" cellulose acetate.

The dope is filtered in the next stage of the process, to ensure clear passage through the jets. After filtration the dope is heated and extruded through jets which contain varied numbers of microscopic holes. From the jets the dope passes through a heated cabinet to evaporate the solvent. As the dope dries it becomes acetate or triacetate yarn.[2,3]

Acidity problems are prevalent because there is a tendency for the methylene chloride/methanol solvent (91:9 v/v) to decompose to form hydrochloric acid when water is present in the system. Formation of hydrochloric acid causes corrosion in the mixers and presses.[4]

In an aqueous solution, several characteristics are known to be true about acids and bases. That is, an acid reacts with base to form a salt, gives a sharp taste to water, and causes litmus to turn red; and a base produces a salt with an acid, gives a bitter taste to water and causes litmus to turn blue.

In the late 1800's Arhennius proposed a theory defining acids as hydrogen containing substances that dissociate into hydrogen ions and anions when dissolved in water, and bases as compounds containing hydroxyl groups that give hydroxide ions and cations.[5,6]

In 1923 Bronsted and Lowry proposed a more generalized concept of acids and bases.[5,7] In their view an acid is any substance capable of accepting a proton and a base is any substance that can donate a proton.

Another view on acids and bases was proposed by Lewis, who defined an acid as an electron pair acceptor and a base as an electron pair donor.[5,6]

Most acid-base work today is based on the latter two theories. However, for useful applications in analytical chemistry the Bronsted-Lowry theory is more applicable.[5]

The easiest way of measuring the amount of unknown acid or base present in solution is through titration. Generally, acid-base tritration is done with the help of indicators. When the endpoint is reached there is an abrupt color change corresponding to the pH range of an indicator.[7,8]

When difficulties arise from aqueous solutions, nonaqueous systems are employed. Indicator dye is affected differently by each solvent, but conditions in aqueous medium are most simulated by the behavior of an indicator in a solution diluted with water. This applies to methyl and ethyl alcohol solutions. In an anhydrous alcohol medium the changes are more pronounced. The effect of the alcohol is shown not only in the intensity of the color, but also in the shade.[9]

The research described in this thesis was concerned with the development of a new method or modification of an existing method for the determination of the acidity in dull cellulose triacetate dope.

In the existing method the indicators Phenolphthalein (1.0%) and Bromothymol Blue (0.04%) were used. The endpoints of these indicators were hard to see, therefore studies were done to improve this. These studies included using Bromothymol Blue (0.04%, 0.16% and 1.0%); Phenol Red (0.02% and 0.16%); Thymolphthalein (0.2%) and Cresol Purple at (0.1%) as indicators.

The standard deviation of the acidities measured show that titrations with Phenol Red (0.16%) as the indicator gave the best results.

EXPERIMENTAL

Reagents

Bromothymol Blue. A 0.04% solution was made by dissolving 0.428 g of the salt in 1000 ml of methanol, a 0.16% solution was made by dissolving 1.712 g of the salt in 1000 ml of methanol and a 1% solution was made by dissolving 10.7 g of the salt in 1000 ml of methanol. Bromothymol Blue was obtained from Matheson, Coleman and Bell Chemical Company.

Phenol Red. A 0.02% solution was made by dissolving 0.225 g of the salt in 1000 ml of methanol, and a 0.16% solution was made by dissolving 0.92 g of the salt in 1000 ml of methanol. Phenol Red was obtained from Matheson, Coleman and Bell Chemical Company.

Cresol Purple. A 0.1% solution was made by dissolving 1 g of the salt in 1000 ml of methanol. This indicator was obtained from Matheson, Coleman and Bell Chemical Company.

Thymolphthalein. A 0.2% solution was made by dissolving 0.2 g of thymolphthalein in 100 ml of methanol. This indicator was obtained from Eastman Organic Chemicals.

Sodium Hydroxide (NaOH). A 0.02 N solution was made by dissolving 0.8125 g of NaOH pellets in a 1:1 methanol/water (%w/v) solution and in a 100% methanol solution. The NaOH was standardized with the aid of a standardette equivalent to 40 ml of 0.2 N sulfuric acid.

Methylene chloride/methanol. This mixture was prepared by adding 91 parts of methylene chloride to 9 parts methanol.

Procedure

The dull triacetate dopes (Arnel) used in this determination work were taken from batches supplied by the Extrusion Department of the Celanese Fibers Company in Rock Hill, South Carolina.

Determination of Acidity of Cellulose Triacetate Dope. To a 250 ml ground glass-stoppered Erlenmeyer flask 100 ml of methylene chloride/methanol solvent (91:9 v/v) was added. Approximately 10 g of dull cellulose triacetate dope (Arnel) was added to the flask. The flask was placed on a Burrell Wrist Action Shaker and allowed to shake until it was throughly mixed. This took about ten to fifteen minutes. Then a few drops of indicator (20) were added. A blank consisting of the same amount of methylene chloride/methanol solvent and indicator used in the sample was also prepared to account for any errors in over-titration.

Samples made by the above procedure were titrated manually and automatically.

The samples were automatically titrated by a Metrohm Potentiograph Titrator E-436. Using Phenol Red as indicator, pH vs. ml was recorded as alcoholic NaOH was added to the samples automatically. The endpoint was reached when an intense pink or red color appeared.

Several different indicators were used in the manual titrations. These included Cresol Purple (0.1%) Thymolphthalein (0.2%), Bromothymol Blue (0.04%, 0.16%, and 1.0%) and Phenol Red (0.2% and 0.16%). The samples were titrated rapidly to their endpoint with 0.02 N NaOH. The endpoint was reached when the color change persisted for thirty to forty seconds.

pH vs. time on methylene chloride/methanol solvent. To a 250 ml beaker 100 ml of methylene chloride/methanol was added. The beaker was covered with a piece of filter paper. A slit was cut into the filter paper for the electrode and pH vs. time was measured by a Beckman pH meter.

In another study, the beaker was covered with filter paper and aluminum foil to form a tighter seal. Again the pH was measured vs. time using a Beckman pH meter.

RESULTS AND DISCUSSION

The acidity of cellulose triacetate dope is a measure of its free acid content or of the free acid produced by decomposition. It is calculated as milliequivalents of acid per 100 g of sample using the following formula:

$$\text{Meq} = \frac{(\text{ml of NaOH used in sample} - \text{ml of NaOH used in blank}) \times N \times 100}{\text{wt of sample}}$$

In the original method for finding the acidity in dope Bromothymol Blue (0.04%) and Phenolphthalein (1.0%) were the indicators used. There were problems connected with visually seeing the endpoint using these indicators.

In steps leading to modification of the original method Bromothymol Blue at different concentrations was studied. These concentrations were 0.04%, 0.16%, and 1.0%. Normally, a 0.1% or a 0.04% indicator solution is used for titration purposes. Since Bromothymol Blue is slightly soluble in water the indicator is dissolved in a small amount of methanol and diluted to the mark with water.

In the preparation of the 0.04%, 0.16%, and 1.0% indicators, the indicators were completely dissolved in methanol. All of the indicators were made in completely alcoholic solutions to keep as much water out of the titration as possible.

During the actual titration with NaOH in a 1:1 methanol/water mixture, indicator began separating from the sample causing two layers to be formed, presumably an aqueous layer which was the top layer formed and a sample layer. In the NaOH there were no separations. After sitting overnight the sample remained thoroughly mixed.

Tables 1, 2, and 3 show the results from titrations with Bromothymol Blue at concentrations of 0.04%, 0.16%, and 1.0%. The more concentrated indicator (1.0%) gave the brightest color and the best visible shade of blue, but statistical data shows that the 0.04% indicator used in a 1:1 methanol water solvent gave the best precision (see Table 4).

Titration in anhydrous media showed that 0.16% gave the highest acidity of the three indicators. The reasons all 3 indicators gave different acidities is unknown. The acidities should have been about the same since the samples were titrated to the same color as the blank and the amount of NaOH used for the blank was subtracted from the amount of NaOH used for the sample to account for errors in overtitration. The amount of NaOH used for the triacetate blank and sample is shown in Table 1. The mls of NaOH used to determine the endpoint of the blank and sample differs by a factor of about 1 ml using either the 1:1 methanol/water NaOH mixture or the completely alcoholic NaOH. This small difference between the sample and blank endpoints could be a possible cause for the variation in acidities. The results from the Phenol Red indicator are shown in Tables 5 and 6. The acidities found using NaOH in a 1:1 methanol/water mixture show that 0.02%, gave the higher acidity value. On the other hand, statistical data shows that 0.16% indicator using NaOH in 1:1 methanol H_2O solvent gave the best precision (see Table 4). With this indicator there was a sharp color change and great color intensity.

Cresol Purple dissolves readily in methanol and is only slightly soluble in water. A 0.04% aqueous solution of the sodium salt is normally used as indicator solution, but for this study a 0.1% solution in methanol was used. This indicator did not give a very clear endpoint. There was not a smooth color transition. The results from this transition are shown in Table 7.

Table 1. Acidity using Bromothymol Blue (0.04%) as indicator.

Sample No.	mls NaOH in methanol used for blank	mls NaOH in methanol used for sample	Acidity found by titration with 0.02 N NaOH in methanol	mls NaOH in equal amounts of methanol and H_2O used for blank	mls NaOH in equal amounts of methanol and H_2O used for sample	Acidity found by titration with 0.02 N NaOH in equal amounts of methanol and H_2O
1	2.05	2.60	0.147	10.37	11.82	0.325
2	2.05	3.20	0.268	10.37	11.87	0.318
3	2.05	3.50	0.331	10.37	11.83	0.351

Table 2. Acidity using Bromothymol Blue (0.16%) as indicator.

Sample No.	Acidity found by titration with 0.02 N NaOH in methanol	Acidity found by titration with 0.02 N NaOH in equal amounts of H_2O and methanol
1	0.711	0.399
2	0.726	0.118
3	0.697	0.123
4	0.791	0.394

Table 3. Acidity using Bromothymol Blue (1%) as indicator.

Sample No.	Acidity found by titration with 0.02 N NaOH in methanol
1	0.62
2	0.66
3	0.547
4	0.646
5	0.595

Table 4. Statistical Data.

Indicator	Standard Deviation
Bromothymol Blue (0.04%)	
NaOH 1:1 methanol/water	0.017
NaOH anhydrous	0.093
Bromothymol Blue (0.16%)	
NaOH 1:1 methanol/water	0.160
NaOH anhydrous	0.041
Bromothymol Blue (1.0%)	
NaOH anhydrous	0.045
Phenol Red (0.02%)	
NaOH anhydrous	0.027
Phenol Red (0.16%)	
NaOH 1:1 methanol/water	0.014
NaOH anhydrous	0.063
Cresol Purple (0.1%)	
NaOH 1:1 methanol/water	0.041
NaOH anhydrous	0.061
Thymolphthalein (0.2%)	
NaOH anhydrous	0.030

Table 5. Acidity using Phenol Red (0.02%) as indicator.

Sample No.	Acidity found by titration with 0.02 N NaOH in methanol
1	0.486
2	0.472
3	0.423
4	0.474
5	0.437

Table 6. Acidity using Phenol Red (0.16%) as indicator.

Sample No.	Acidity found by titration with 0.02 N NaOH in methanol	Acidity found by titration with 0.02 N NaOH in equal amounts of H_2O and methanol
1	0.362	0.197
2	0.314	0.191
3	0.238	0.17

Table 7. Acidity using Cresol Purple (0.1%) as indicator.

Sample No.	Acidity found by titration with 0.02 N NaOH in methanol	Acidity found by titration with 0.02 N NaOH in equal amounts of H_2O and methanol
1	0.139	0.354
2	0.114	0.326
3	0.024	0.273

Thymolphthalein is nearly insoluble in water, but readily soluble in methanol. For most titration purposes this indicator is usually dissolved in alcohol and diluted to the mark with an equal amount of water. For this study a 0.2% solution in methanol was used. The color intensity of this indicator fades when left to stand; therefore, it was concluded that Thymolphthalein would not be a good indicator to use when comparison studies are conducted. The results from this indicator are shown in Table 8.

Standard deviations were calculated to obtain the variability of the determinations. Standard deviation is a measure of the precision of the instrument.

$$\sigma = \left(1/n-1 \sum_{i=1}^{n} (x_1 - \bar{x})^2 \right)^{1/2}$$

The standard deviations were calculated using the Prophet System.

Based on the statistical data shown in Table 6 and the sharp color change of the indicator at the endpoint it was concluded that Phenol Red at (0.16%) using NaOH in a 1:1 methanol water solvent was the best indicator for determining the acidity.

An automatic titrator was also used to check the results between manual and automatic titrations. Phenol Red was used as the indicator to determine whether the equivalence point and the endpoint were at the same point. The results are shown in Fig. 1. No equivalence point was found.

Table 8. Acidity using Thymolphthalein (0.2%) as indicator.

Sample No.	Acidity found by titration with 0.02 N NaOH in methanol
1	0.416
2	0.361
3	0.388
4	0.346
5	0.409

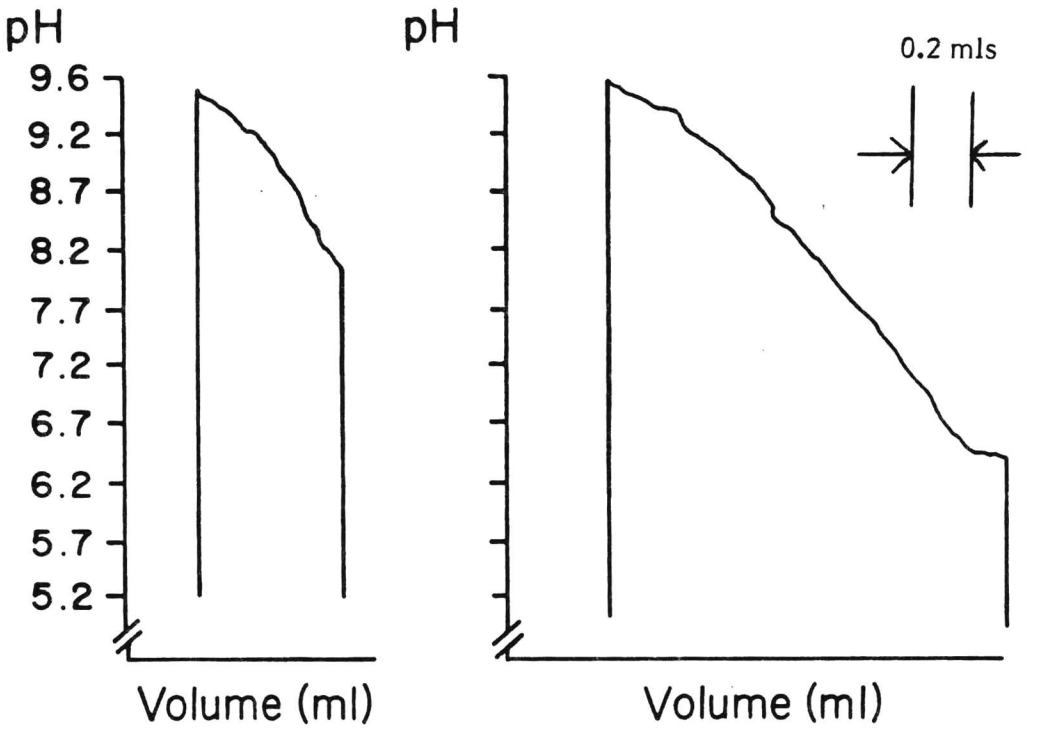

Fig. 1. pH of blank solution and triacetate solution vs. volume of titrant using an automatic titration.

The initial and final pH's of the triaetate solution sample and a blank solution are shown in Figs. 1 and 2. The initial pH of the blank solution was higher than the pH of the sample solution. This showed that adding cellulose triacetate dope to the solvent made the solution acidic. However, the final pH endpoint of the blank was found to be about the same as the endpoint of the sample solution. Therefore, we concluded that determining the final pH of the triacetate solution would probably be suitable as a procedure for determining the acidity.

A study was also conducted to find the reasons for the wide range of acidities obtained when samples from the same batch of triacetate dope were used.

The pH of the methylene chloride/methanol mixed solvent was measured over a period of time. The results are shown in Table 9.

In one study, the beaker containing the solvent was covered with filter paper. The pH changed approximately 2 pH units over a 20 min interval. In another study filter paper as well as aluminum foil were used to cover the beaker to form a tighter seal. The pH only changed one pH unit here. Plots of pH vs. time are shown in Fig. 2.

The graphs show changes in acidity with time probably due to solvent evaporation or contamination from the atmosphere.

Solvent evaporation or contamination could have been the cause of the variation in acidity values since the solvent and solution were exposed to the atmosphere at three stages: when the dope was added, when the indicator was added and during the actual titration. The total exposure time was approximately 5 minutes. The graph showed changes with time possibly due to contamination from the atmosphere or to electrode equilibration.

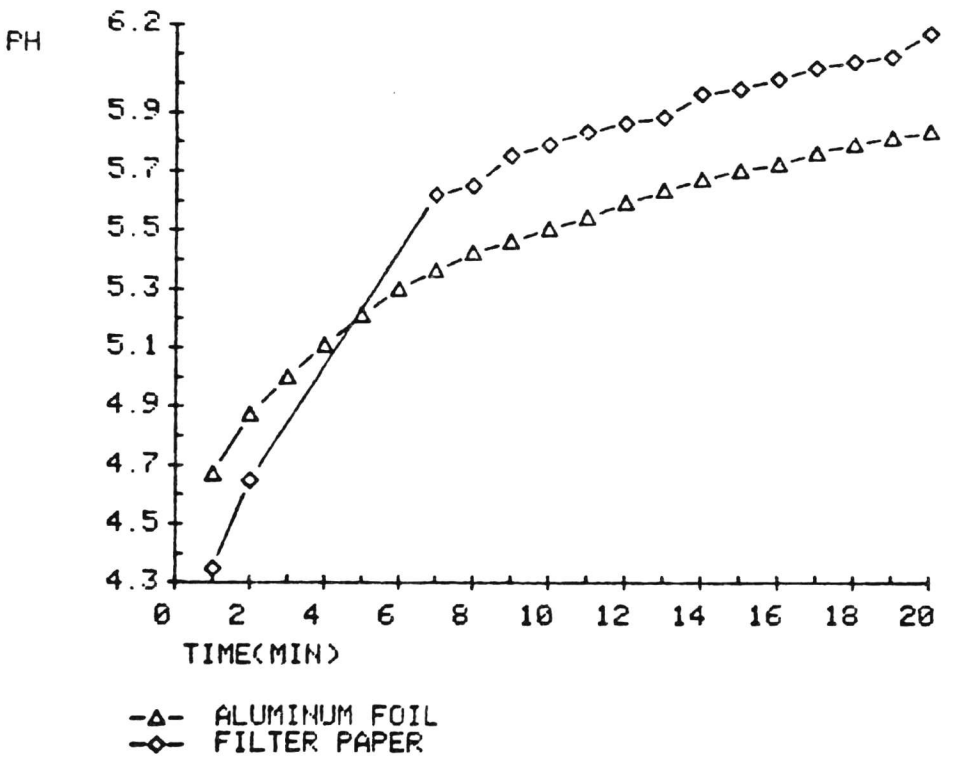

Fig. 2. pH vs. time of methylene chloride/methanol solvent.

Table 9. pH vs. time of methylene chloride/methanol solvent.

Time (min.)	pH[a]	pH[b]
1	4.35	4.67
2	4.65	4.87
3	-	5.00
4	-	5.11
5	-	5.21
6	-	5.30
7	5.62	5.36
8	5.65	5.42
9	5.75	5.46
10	5.79	5.50
11	5.83	5.54
12	5.86	5.59
13	5.88	5.63
14	5.96	5.67
15	5.98	5.70
16	6.01	5.72
17	6.05	5.76
18	6.07	5.79
19	6.09	5.81
20	6.17	5.83

[a]Beaker sealed with filter paper.

[b]Beaker sealed with filter paper and aluminum foil.

Solvent evaporation as a cause for variable acidities was considered but did not seem reasonable because there was no appreciable change in volume and the change in pH was in the opposite direction to that expected if evaporation occurred.

CONCLUSION

The acidity of cellulose triacetate dope can be determined by using Phenol Red as the indicator. Based on standard deviation calculations this indicator gave the best results, however, the lack of reproducibility of the Meq in this study suggest further work is needed.

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